

Quantum Size Effect and Electronic Stability of Freestanding Metal Atom Wires

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Abstract

Fabrication of freestanding or supported metal atom wires may offer unprecedented opportunities for investigating exotic behaviors of one-dimensional systems, including the possible existence of non-Fermi liquids. Many recent efforts have been devoted to the formation of different kinds of metal atom wires in freestanding forms by novel techniques like mechanical break junction or deposited on substrates via self-assembly, focusing on their mechanical, chemical and electronic properties. Various atom wires with different lengths can be obtained during fabricating processes. Their size distributions have been extensively analyzed, which exhibit diverse features. Although several factors such as strain and substrate effects have been employed to interpret these phenomena, the stability of atom wire itself is largely ignored. Using density functional theory calculations, we present a thorough study on freestanding metal atom wires, including *s*, *sd* and *sp* electron prototypes, to examine the size effect in their stabilities. We find that the total energy of all systems oscillates within wire length, which clearly indicates the existence of some preferred lengths. Increasing the length of atom wires, *s* electron system shows even-odd oscillation following a $a/x + b/x^2$ trend in the stability, due to both electrons pairing up and one-dimensional quantum confinement. Meanwhile, *sd* electron systems show a similar oscillation within wire length although *s-d* hybridization is presented. In *sp* electron systems, some oscillations beyond the even-odd one are exhibited due to unpaired *p* orbitals resulting in some nontrivial filling rule. Our findings clearly demonstrate that electronic contribution is quite critical to the stability of freestanding atom wires and is also expected to dominate even when atom wires are deposited on substrates or under strain. This study sheds light on the formation of metal atom wires and helps understanding relevant phenomena.

I. INTRODUCTION

As a model of one-dimensional (1-D) systems, metal atom wires have attracted enormous attentions to investigate relevant exotic 1-D behaviors, including the existence of non-Fermi liquids[1, 2]. Various experimental techniques have been developed to fabricate different kinds of metal atom wires. There have been many reports that atom wires can be self-assembled or manipulated on semiconducting or metallic substrates, such as Au/Si(111), Au/Si(557), Ag/Si(557), Pb/Si(557), Ga/Si(100) and In/Si(111)[1–10]. Furthermore, free-standing atom wires have also been obtained via some novel methods such as mechanical break junctions (MBJ)[2, 11]. All these progresses greatly spark diverse investigations on properties/behaviors of metal atom wires. For example, Segovia *et al.* measured band structure of Au/Si(557) by angle-resolved photoemission spectroscopy (ARPES), and suggested the existence of a Luttinger liquid[4]. A later work on temperature-dependent ARPES and scanning tunnel microscopy study showed there is a symmetry-breaking metal transition in Au/Si(557) which can be interpreted as a traditional Peierls transition, precluding the formation of a Luttinger liquid at low temperature[12]. In addition, a recent measurement by electron energy loss spectroscopy revealed significant dynamic exchange correlation effects on the 1D plasmon despite its high electron density and large Fermi velocity[13]. Using MBJ technique, Yanson *et al.* explored Au atom wires, and found a wire with 7-atom length can be formed which behaves as a perfectly quantized one-dimensional conductor[11]. All these investigations clearly demonstrate that metal atom wires are desirable workhorses to testify theoretic predictions of 1-D systems.

To explore these exotic properties of 1-D systems, longer or defect-free metal atom wires are quite critical. Therefore, understanding the formation mechanism of these wires should help to improve our ability to control the fabrications such as formation wires by different materials and longer ones. Smit *et al.* gave a systematic study over 5d metals by employing MBJ, and suggested a stronger bonding of low-coordination atoms with respect to 4d metals is due to *sd* competition caused by the relativistic effects[14]. Moreover, sequential theoretical simulations confirmed that 5d metal atom wires like Au and Pt have bonds much stronger than their bulk ones[15]. Given supported atom wires, a highly anisotropic substrate as the growth template is very important. Usually, surfaces with a periodic step structures like vicinal metal or semiconductor surfaces are employed in molecular beam epitaxy to fabricate

arrays of atom wires. Once adatoms diffuse anisotropically on these surfaces, well-ordered 1-D atom wires are possibly self-assembled[16, 17].

Strictly speaking, there are no ideal 1-D systems like infinite atom wires exist in experiments but segments of different lengths obtained in fabrications. Such wires of varying lengths have been observed in some heteroepitaxial self-assembled systems and MBE experiments[1, 11]. The length distribution can affect the phase transition temperature, change the conductivity, inhibit charge orders, and alter the effective dimensionality of the system. Thus, it is essential to understand the factors leading to different sizes and to control the wire lengths. So far, a few works have suggested the length distribution generally depends on several factors including the deposition coverage, the substrate temperature, adatoms adsorption energy and surface defects[17–23]. With respect to different metal atom wires, the length distributions showed quite different behaviors. Some experimental works reported that the length distributions of Ga and In atom wires on Si(100) surface monotonously decrease for various coverages, and have certain scale relations[17, 18]. Comparing with experimental data of Ag wires on Pt(997) surface, Gambardella *et al.* examined the size distribution of atom wires in the framework of 1-D lattice gas model, and found that the lengths obey the geometric distribution[21]. This length distribution indicated that an atom binding to the wire is independent of its length, thus suggesting only nearest-interactions account for its growth. A later work by Tokar *et al.* showed that incorporating additional interactions like elastic strain and charge transfer can obtain higher accurate fitting results[20]. Whereas, an extensive analysis based on STM by Crain *et al.* found an oscillating length distribution is exhibited in Au/Si(553)[24]. They ascertained short-range interactions like local rebonding of the surface result of a strong peak at a length of one atom, and found that even wire lengths are favored over odd lengths up to lengths of at least 16 atoms, which indicates the quantum size effect plays an important role. This growth feature is in analogy to the electron growth of thin film[27], which implies pure electronic contribution can exert a fundamental impact on wires' growth. Further theoretical analysis by Souza *et al.* suggested a model only within electronic structure can capture the feature of the even-odd oscillation, and qualitatively agreed with the experimental length distribution[25].

As revealed in both experiments and preliminary tight-binding calculations, the quantum size effect can dominate Au atom wire's growth[24, 25], and result of an even-odd oscillation. Except Au system, few attentions have been given for the other metals about this aspect.

Hence, it should be interesting to explore how other metal atom wires are modulated by the quantum size effect and some relevant impacts on their stabilities. Our purpose is to present a systematic *ab initio* study on the quantum size effect in linear metal atom wires' stability, with a special focus on its development with wire length. We choose several prototypes of *s*, *sd* and *sp* electron systems such as Na, Ag, Au, Ga, In and Pb atom wires in freestanding form for these atom wires all have been obtained experimentally[1, 2]. We hope our study will facilitate the understandings of various size distributions even under the influence of substrates, strain and charge transfer. We find that the total energies of all systems oscillate within wire length, which clearly indicates the existence of some preferred lengths. In particular, *s* electron system shows an even-odd oscillation following a $a/x + b/x^2$ trend in the stability when the length is increased, which results from the pair-up of electrons and 1-D quantum confinement along the wire. Meanwhile, *sd* electron systems show a similar oscillation with the wire length although *s-d* hybridization occurs. In *sp* electron systems, some beyond even-odd oscillations are exhibited as unpaired *p* orbitals result in some nontrivial filling rule, which almost washes out the effect of 1-D confinement because of their localized bonding characteristics.

The rest of this paper is organized as follows. The computational methods and numerical details are presented in Sec. II. Sec. III gives the results of various metal atom wires. The quantum size effect and electronic stability are studied in detail. A brief summary is then given in Sec IV.

II. CALCULATION METHODS

All results we present here were carried out by the projector augmented-wave(PAW) method[29] implemented in the Vienna *ab initio* simulation package(VASP)[30, 31]. Based on density-functional theory(DFT), exchange and correlation effects were described by the generalized gradient approximation(GGA-PBE)[32]. The energy cutoff for plane-wave basis of 300.0 eV was used for all examined systems, which ensured the total energy converging into 0.01 eV per atom. In particular, we employed a small Gaussian broadening width 0.01 eV to achieve integer occupation of states. Isolated atom wire was simulated in a rectangular box with periodic images' separation larger than 10 Å, and the longest one was up to 20 atoms for each metal. As for relevant infinite systems, we sampled 1-D Brillouin zone

within 40 Monkhorst-Pack grids after carefully checking the convergence of k-point sampling. Here, we adopted one atom per unitcell without explicit consideration of Peierls effect since further checks on the two-atom unitcell neither showed any apparent dimerization nor made any difference in bandstructure but just folded up the 1-D Brillouin zone. All geometric structures were relaxed using the conjugate gradient method until residual force per atom was less than 0.01 eV/ Å .

Since 1-D atom wires are likely to be metastable for all involved metals, here we adopted initial configurations for atom wires by setting bond lengths to that of the infinite one. Because of certain fine interactions resulting from magnetic coupling for *sd* and *sp* electron systems, it is impossible for us to conduct a thorough study of various combinations over initial magnetic moments of atoms to obtain a local minimum, especially for a wire of tens of atoms. Although there are some ambiguities in energy minimums of atom wires, these fine interactions are unlikely to yield major changes or affect dominant electronic interactions between atoms. So we used several simple combinations within initial magnetic moments of atoms like $\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$ (ferromagnetic), $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$ (antiferromagnetic), $\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow$ (antiferromagnetic), $\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow$,etc. for 6-atom wire in further geometric relaxation, and chose the energy minimum among them. A similar setting for initial conditions of different magnetic moments has been discussed in previous work on transition metal atom wires while examining average cohesive energy of various lengths[26]. Our calculation results showed energy uncertainty of the minimum is less than 0.1 eV (about 0.01 eV per atom), ensuring us to reach further conclusions.

To characterize the electronic stability of atom wires and the corresponding size effect, we use the cohesive energy[27, 28],reading

$$E_c(n) = (E_t(n) - n \cdot E_t(1))/n, \quad (1)$$

to examine atom wires' stability in different length, where $E_t(n)$ is the total energy of the atom wire of n atoms. Thus, the larger the absolute value of cohesive energy is, the more stable the wire segment will be. This energy value purely reflects the contribution of electronic binding interaction between atoms. We then introduce the second difference of $E_{c,reading}$

$$d^2 E(n) = E_c(n+1) + E_c(n-1) - 2 \cdot E_c(n), \quad (2)$$

as the criterion for the stability of a *sp* metal wire segment in analogy with that for a thin film[27]. According to Eq.(2), a wire of n atoms is stable when $d^2E(n) > 0$ and unstable otherwise.

III. RESULTS AND DISCUSSIONS

A. Na atom wires

Firstly, we consider Na atom wires. So far, considerable attention in Na wire has been drawn to its electron transport properties, especially to its quantum conductance measurements[2]. Yanson *et al.* experimentally studied the conductance through Na thin junction via MBJ technique, and found the conductance histogram shows a typical oscillation on measured times due to the shell effect, a pure electronic effect resulting from size confinement[33]. Further theoretical works were then extended to situations of atom wire[34, 35, 37], and calculated conductance showed an oscillation with wire length, which also largely depended on the structure of nanocontacts[36, 37].

Since sodium has only one valence, the stability of atom wires would be greatly enhanced once electrons pair up. The cohesive energy therefore shows an even-odd oscillation with the length, as shown in Fig.1(a). It is clear that the pair-up of electrons is much more pronounced for shorter wires, and gains small energy less than 0.01 eV when the length is up to 10-atom or more. Thus, relevant even-odd oscillation would be smeared off for longer wires, which suggests the quantum size effect can not be easily observed in the experiment as a bit strain or charge transfer is supposed to wash out the related oscillation. Actually, the cohesive energy converges in a $a/x + b/x^2$ trend as the length increases, here x is the wire length, and a, b are constants. This trend is simply caused by the quantum confinement along the wire direction, since the energy level E_i of a 1-D square quantum well is inversely proportional to the square of its width W , i.e, $E_i \sim i^2/W^2$, as already shown in a particle-in-a-box model. As a result, the total energy of n electrons is the sum over the energy levels and proportional to $n(n+1)(2n+1)/n^2$ given $W \sim n$. Therefore, the cohesive energy per electron follows the $a/x + b/x^2$ trend in this simple model. This remarkable agreement between *ab initio* results and the particle-in-a-box model is clearly due to the delocalized and unidirectional dependence of the s orbitals of Na atom wires. The highest occupied wire

state (HOWS) for 6-atom wire is then presented in Fig.1(c), showing a typical $ss\sigma$ binding character with two nodes along wire. Clearly, the number of nodes in HOWS depends on the wire length, with $(n - 1)/2$ for odd one while $(n - 2)/2$ for even situation, stemming from the orthogonality relations between the wavefunctions.

B. Ag and Au atom wires

Recently, both Ag and Au atom wires were fabricated experimentally. It was reported that ultrathin silver wires with a width 0.4 nm were successfully synthesized inside nanotubes[38]. Some MBJ techniques and atom manipulation by STM were extended to both Ag and Au systems for fabricating nanowires[9, 11, 14, 39, 40]. In this case, the structure of nanowire is likely to be a linear atom wire. In addition, some experimental efforts have been devoted to depositing Ag atom wire in Si vicinal surface[10]. All these experimental progresses encouraged extensive theoretic studies on various aspects of Ag atom wires, especially on electric properties and quantum transport[2, 41, 42]. With regard to Au atom wire, there have been enormous works exploring its various properties since its first experimental fabrication[1, 2, 11, 43]. A few attempts have been devoted to the study of its transport properties by MBJ techniques, and showed Au atom wire can survive in a longer length in comparison with Ag system due to stronger sd competition[11, 14]. Many efforts have also focused on possible realizations of Luttinger liquids and other 1-D exotic behaviors by depositing Au atom wires in various vicinal surfaces such as Si(553), Si(557), Si(337), Ge(100)[1, 6, 24, 44]. All these works boost several seminal explorations such as end modes of 1-D systems and atom wires' electronic growth[24, 44, 45]. And experimentally, both Ag and Au atom wires showed size effects can largely modulate their electronic properties and stability[24, 40].

Silver is of the closed $4d$ shell, behaving as a single valence system. As displayed in Fig.1(b), the cohesive energy of Ag atom wires shows a similar even-odd oscillation as that of Na atom wires, and relevant values are around -1.0 eV. Since certain sd hybridization is likely to enhance the binding interaction between atoms, Ag atom wires show a bit larger amplitude of the even-odd oscillation in comparison with Na atom wires. This enhanced interaction should lead to observing relevant quantum size phenomena in real experiments. Actually, recent STM measurements have revealed that resonances of unoccupied states show

a strong size dependence of energy values on Ag/Ag(111) system[40], which suggests the size effect survives even under the influence of substrate. Therefore, we can expect relevant quantum size effects would exhibit in some self-assembled Ag wires. And we present HOWS for 6-atom wire in Fig.1(d), which clearly shows a bit different character from that of Na atom wire due to some sd hybridization. Meanwhile, the number of nodes of HOWS is also the same as that of Na systems.

In contrast to Ag, relativistic effects are quite large in Au system, which result in strong sd competition. Consequently, the s shell is contracted and the d electrons move up in comparison with Ag. This electronic feature leads to stronger binding interaction in Au wires, and the cohesive energy approaches -1.5 eV when the length is increased as shown in Fig.2(a). When the length is shorter than 13 atoms, the cohesive energy shows almost the same behavior as that of the Na and Ag wires. However, a crossover occurs when $n = 13$, leading to a transition of the oscillation. This behavior can be interpreted by the bandstructure of infinite wire as shown in Fig.2(b) and (c). Due to the axial symmetry, d bands split into 3 branches, e.g, d_{z^2} , $d_{x^2-y^2}/d_{xy}$ and d_{xz}/d_{yz} . Then, four band branches below the Fermi level are shown in Fig.2(c), respectively. At Γ point, the lowest band branch is mostly of the d_z character, which then develops across 1-D Brillouin zone by approaching the Fermi level at K point. However, $d_{x^2-y^2}/d_{xy}$ branch is almost a flat band across 1-D Brillouin zone. This dispersionless character suggests there are no bonding interaction between the $d_{x^2-y^2}/d_{xy}$ electrons of atoms and they are just localized around Au atom itself. The next band branch, crossing the Fermi level at the middle of 1-D Brillouin zone, is mostly of the s character. The last branch, d_{xz}/d_{yz} , is then in the vicinity of the Fermi level at Γ point. At Γ and K , two special symmetric points of 1-D systems, the band dispersions are all horizontal, leading to very sharp van Hove singularities of 1-D system which result in sharp peaks of density of states(DOS) as displayed in Fig.2(b). Since the bands mostly have d character at the edges, the exchange energy gain could be rather large when a band spin splits so that one of the spinchannels band edges up above the Fermi level, and the other then downs below. Thus, if a band edge ends up sufficiently near the Fermi level, e.g., appearance of sharp peaks of DOS, we can predict a magnetic moment [46], which is known as the Stoner instability. Meanwhile, this instability depends closely on Au bond length, and a bit elongating(shortening) bond can eliminate(enhance) the related ferromagnetic behavior as also reported in previous works[46]. Such behaviors mean the bond lengths of Au wires

will affect significantly the positions of band edges. As for finite wires of different lengths, bonds oscillate around that of infinite one. Correspondingly, their HOWSs show different characters. When the wire length is less than 4-atom, bonds are smaller than that of infinite wire (2.59 Å), and HOWSs are of the d_{z^2} character, partially with the s contribution. 4-atom wire is of two bonds less than 2.59 Å, large part of HOWS also shows d_{z^2} character. Longer than the number of 4-atom, central bonds of atom wires are then a bit longer than 2.59 Å, and HOWSs show d_{xz}/d_{yz} character accordingly. When Au atom wire grows up to a certain length, the exchange energy gain thereby can split spin channels of d_{xz}/d_{yz} orbitals, and cause a crossover of stability of Au wire when $n = 13$ as shown in Fig.2(a). As a result, the corresponding HOWSs change to s character, in partial hybridization with d_{z^2} orbitals.

However, previous reports indicate there is only one conduction channel around the Fermi level[2], which suggests the emergence of d_{xz}/d_{yz} bands edges around Fermi level for the infinite wire are problematic and may account for the above crossover of the cohesive energy. Moreover, strong localized $d_{x^2-y^2}/d_{xy}$ orbitals also mean that relevant self-interaction errors(SIE) cannot be ignored for 1-D wires[47]. We then employed GGA+U scheme to shift the d bands and remove related SIE for verifications. As shown in Fig.2(d) and Fig.2(e), even a small $U_{eff}=1.0$ eV can eliminate Stoner instability as no sharp DOS peaks emerge around the Fermi level, and relevant crossover at $n = 13$ atoms vanishes at the meantime. Correspondingly, the HOWSs of different wires bear a similar characteristics with contribution of hybridized states between s and d_{z^2} . As displayed in Fig.2(d),(h), HOWSs of 6-atom wire from GGA and GGA+U calculations are given, respectively. Obviously, GGA result shows a d_{xz}/d_{yz} character, while GGA+U results of a $s + d_{z^2}$ hybridization orbital. These results clearly indicate that improper descriptions on the d bands may lead to the ferromagnetic behavior of the infinite wire and the crossover of the finite wires stability. As revealed in Fig.2(e), the cohesive energy also follows the $a/x + b/x^2$ trend well. Thus, the relativistic effects do not make much difference between stability trends of the Au and Ag wires but enhance binding interactions between Au atoms. This stronger binding property makes quantum size effects of Au wires more easily perceptible in experiments, even under the influence of charge transfer or strain effect. As reported in the experimental work by Crain *et al.*, an even-odd oscillation exhibited in Au/Si(553) system at least up to 16 atoms[24]. Many relevant properties due to quantum size effects of Au atom wires are therefore both theoretically and experimentally predictable.

C. Ga, In and Pb Atom Wires

Bulk Ga, In and Pb are typical p electron metallic systems, and large efforts have been devoted to the formations of their corresponding atom wires in different vicinal surfaces to investigate the effect of p electron in 1-D systems[1, 5, 7, 8, 17, 18]. These atom wires showed some new behaviors in comparison with s , or sd systems. Typically, the length distributions of Ga and In atom wires on Si(100) surface decrease monotonously for various coverages, and show some scale relations[17, 18]. Thus, it is of great interest to explore how the pure electronic contributions affect their length distributions.

We focus on Ga and In atom wires first. Both gallium and indium have 3 valences: 2 s electrons and 1 p electron in the outmost shell. Because of the large energy difference between the s and p electrons, little s - p hybridization exhibits in these two elements as revealed by the bandstructures of the infinite wires in Fig.3(a) and (d), and the stability of relevant atom wires is thus dominated by the p electrons. The bandstructures of Ga and In atom wires are quite similar, particularly for the valence bands, and both have three band branches below the Fermi level. Accordingly, the lowest branches are both of the s character. Then, the next one at Γ point is predominated by p_x/p_y electrons, and crosses over the Fermi level. The branch of p_z character is also across the Fermi level about K point. Hence, the combination of p_z orbitals of atom wire forms $pp\sigma$ bonds, and p_x/p_y orbitals contribute to $pp\pi$ states. This bonding property results in complicated behaviors of atom wires. As shown in Fig.3(b) and (e), the cohesive energies of Ga and In atom wires both show oscillations beyond the even-odd pattern. Furthermore, the second difference of the cohesive energy d^2E is also shown together, and exhibits a clear picture for the stability of atom wires. It clearly shows that Ga atom wires of 2,3,4,6,8,12,16,18 atoms are stable segments, and In atom wires also give a similar pattern and favor 2,3,4,6,9,12,14,17 atoms. Since there is some uncertainty of 0.01 eV per atom to determine a local minimum for sp systems, some like 10-atom, 14-atom segments of Ga wires or 11-atom, 15-atom segments of In wires probably lean to stable. In other words, d^2E of these wire segments is likely to be positive. Therefore, d^2E of Ga wires would display an even-odd oscillation around zero after 4-atom, which implies that 6-atom, 8-atom, 12-atom, 16-atom, 18-atom, and probably 10-atom, 14-atom are magically stable among others. Meanwhile, d^2E of In wires shows a bit complicated oscillation around zero, and also exhibits some magical sizes such as 6-atom, 9-

atom, 14-atom and 17-atom. This fact would confound experimental observations out of the consideration of environmental factors like the charge transfer, which may lead to different size distributions. Although gallium and indium have the same valence configuration, a bit difference of nuclei radius should result in this distinction in the stability. Actually, gallium and indium have different crystal structures due to the same fact. 6-atom HOWSs of Ga and In systems are then presented in Fig.3(c) and (f), respectively, clearly showing a $pp\pi$ character.

Like gallium and indium, lead also has little sp hybridization when forming the atom wires, which leads to only two p electrons contributing to binding interactions as revealed by the bandstructure of infinite wire shown in Fig.4(a). The valence bands are also similar to that of Ga wire or In wire, with three band branches below the Fermi level. The s band, the lowest branch, is shown about 3.5 eV from p_z branch at K point, while both p_x/p_y and p_z branches cross over the Fermi level in the middle of 1-D Brillouin zone. Due to axial symmetry, $p_{x/y}$ orbitals are two-fold degenerate and contribute to $pp\pi$ states of atom wire while the combination of p_z orbitals forms $pp\sigma$ bonds. Such binding behaviors are quite similar to those of Ga and In atom wires, but involve 2 p electrons per atom to be filled up. Therefore, the stability of Pb atom wires should present a certain oscillation beyond the even-odd feature as displayed in Fig.4(b). And based on the second difference d^2E in Fig.4(b), we find the stable systems are of 2,3,4,6,7,10,11,13,15,18 atoms, respectively. Meanwhile, relative large amplitude of oscillation also suggests this stability trend survives even under environmental influences, within some preferred lengths in fabrications. As for a Pb dimer, two p electrons occupy $pp\sigma$ bond and other two then go into $pp\pi$ bond. Interestingly, HOWS of Pb dimer is $pp\sigma$ bonding state while that of other lengths is relevant $pp\pi$ state. Concerned with 3-atom wire, two electrons go into $pp\sigma$ bond, and the rest 4 p electrons then fully fill up the two-fold degenerate $pp\pi$ bonding state. The full occupation of bonding states makes 3-atom wire inert, and explains why 3-atom wire is stable among others. Thus, when the atom wire becomes longer, more complicated electronic states are required to fill up, contributing to this specific behavior. At the end, HOWS of 6-atom Pb wire is then given in Fig.4(c), showing a typical $pp\pi$ character with a node in the middle of the atom wire.

Results on free-standing atom wires definitely oversimplify the stability trends of 1-D atom wires. The adsorption of atoms on metallic or semiconducting substrates should lead to

certain hybridization of atom orbitals with electronic states of substrates. In fact, the interactions between single atoms in 1-D wires result from a direct overlap between atoms' wavefunctions and substrate-mediated mechanisms, such as the interface Friedel oscillations[27]. Thus, the tradeoff between these two interactions would result in different length distributions in experimental observations. As for the Au atom wires, the strong *sd* hybridization enhances binding interaction between Au atoms, leading to a pronounced even-odd oscillation of stability even for long wires. Consequently, relevant quantum size effect was observed in Au/Si(553) system while few work touches this issue for Na or Ag wires[24]. This behavior implies atom wires with relative large amplitude of oscillations like Ga and Pb are likely to have quantum size phenomenon even under the influence of substrate or strain effect. Therefore, more works are expected to explore relevant quantum size effects in atom wires like Ga and Pb wires.

IV. CONCLUSION

In conclusion, we have given a systematic study on electronic stability and quantum size effect of 1-D metal atom wires by extensive *ab initio* calculations. The results show that the cohesive energy of Na atom wires presents a typical even-odd oscillation with a $a/x + b/x^2$ trend, which can be ascribed to a typical 1-D quantum confinement as well as the pair-up of electrons. Meanwhile, Ag atom wires show a similar behavior but with a stronger binding interaction due to certain *sd* hybridization. A good agreement with the $a/x + b/x^2$ trend actually suggests the hybridized states of Ag are still quite delocalized and unidirectional. As for Au atom wires, short ones that are less than 13 atoms show a similar even-odd oscillation. Once the length increases to 13 atoms, a crossover occurs. Such behavior is due to the emergence of d_{xz}/d_{yz} states into bonding interactions, which also results in ferromagnetic property of the infinite wire caused by 1-D von Hove singularities around Fermi level. Further GGA+U calculations show that even a small $U_{eff}=1.0$ eV can eliminate the relevant crossover when $n = 13$ and the ferromagnetic behavior of the infinite Au wire, which implies a proper description of the *d* states can affect significantly the behaviors of the Au wires. The large *sd* hybridization due to the relativistic effect enhances bindings between the Au atoms, relevant even-odd oscillation thereby can be observed experimentally. With respect to *sp* systems examined here, we find the stabilities of Ga, In and Pb atom

wires are all dominated by binding interactions between the p electrons because of little hybridization between the s and p electrons. Thus, the directional binding behaviors of the p electrons, e.g., $pp\sigma$ due to the combination of p_z orbitals and $pp\pi$ from p_x/p_y orbitals result in intricate oscillations in the stability trends, and suggest relevant status of electrons filling-up determines the dominant behavior.

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- [1] P. C. Snijders and H. H. Weitering, Rev.Mod.Phys. **82**,307 (2010).
 - [2] M. Springborg and Y. Dong, *Metallic Chains/Chains of Metals*, Elsevier(2007).
 - [3] S. C. Erwin and H. H. Weitering, Phys.Rev.Lett. **81**,2296 (1998).
 - [4] P. Segovia, D. Purdie, M. Hengsberger, and Y. Baer, Nature **402**,504(1999).
 - [5] K. S. Kim, H. Morikawa, W. H. Choi, and H. W. Yeom, Phys.Rev.Lett. **99**,196804(2007).
 - [6] I. K. Robinson, P. A. Bennett, and F. J. Himpsel, Phys.Rev.Lett. **88**,096104(2002).
 - [7] P.C. Snijders, S. Rogge, C. González, R. Pérez, J. Ortega, F. Flores and H. H. Weitering, Phys.Rev.B **72**, 125343(2005).
 - [8] C. González, P.C. Snijders, J. Ortega, R. Pérez, F. Flores, S. Rogge and H. H. Weitering, Phys.Rev.Lett **93**,126106(2004).
 - [9] N. Nilius, T. M. Wallis and W. Ho, Science, **297**,1853(2002).
 - [10] J.R. Ahn, Y.J. Kim, H.S. Lee, C.C. Hwang, B.S. Kim, and H.W. Yeom, Phys.Rev.B **66**, 153403(2002).
 - [11] A.I. Yanson, G.Rubio Bollinger, H. E.van den Brom, and N. Agraït and J.M. van Ruitenbeek, Nature **395**,783(1998).
 - [12] J. R. Ahn, H. W. Yeom, H. S. Yoon, and I.-W. Lyo, Phys.Rev.Lett. **91**,196403(2003).
 - [13] T. Nagao, S. Yaginuma, T. Inaoka, and T. Sakurai, Phys.Rev.Lett. **97**,116802(2006).
 - [14] R. H. M. Smit, C. Untiedt, A. I. Yanson, and J. M. van Ruitenbeek, Phys.Rev.Lett. **87**.266102(2001).

- [15] S. R. Bahn and K. W. Jacobsen, Phys.Rev.Lett. **87**,266101(2001).
- [16] N. Oncel, J. Phys.:Condens.Matter **20**,393001(2008).
- [17] J. Javorský, M. Setvín, I. Oštádal, P. Sobo, and M. Kotrla, Phys.Rev.B **79**,165424(2009).
- [18] M. A. Albao, M. M. R. Evans, J. Nogami, D. Zorn, M. S. Gordon, and J. W. Evans, Phys.Rev.B **72**,035426(2005).
- [19] R. B. Stinchcombe and F. D. A. Aarão Reis, Phys.Rev.B **77**,035406(2008).
- [20] V. I. Tokar and H. Dreyssé, Phys.Rev.B **76**,073402(2007).
- [21] P. Gambardella, H. Brune, K. Kern, and V. I. Marchenko, Phys.Rev.B **73**,245425(2006).
- [22] V. I. Tokar and H. Dreyssé, Phys.Rev.E **68**,011601(2003).
- [23] P. Kocán, P. Sobotík, I. Oštádal, J. Javorský, and M. Setvín, Surf.Sci. **601**, 4506(2007).
- [24] J. N. Crain, M. D. Stiles, J. A. Stroscio, and D. T. Pierce, Phys.Rev.Lett. **96**,156801(2006).
- [25] A. M. Souza and H. Herrmann, Phys.Rev.B **77**,085416(2008).
- [26] C. Ataca, S. Cahangirov, E. Durgun, Y.-R. Jang, and S. Ciraci, Phys.Rev.B **77**,214413(2008).
- [27] Z. Zhang, Q. Niu, and C. Shih, Phys.Rev.Lett. **80**,5381(1998).
- [28] J.-H. Cho, Q. Nin, and Z. Zhang, Phys.Rev.Lett. **80**, 3582(1998).
- [29] P.E. Blöchl, Phys.Rev.B **50**, 17953 (1994).
- [30] G. Kresse and J. Furthmüller, Phys.Rev.B **54**,11169 (1996).
- [31] G. Kresse and D. Joubert, Phys.Rev.B **59**,1758 (1999).
- [32] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys.Rev.Lett. **77**,3865(1996).
- [33] A.I. Yanson, I.K. Yanson, and J.M. van Ruitenbeek, Nature **400**,144(1999).
- [34] R.N. Barnett and U. Landman, Nature **387**, 788(1997).
- [35] Y.J. Lee, M. Brandbyge, M.J. Puska, J. Taylor, K. Stokbro, and R.M. Nieminen, Phys. Rev. B **69**, 125409 (2004).
- [36] H.-S. Sim, H.-W. Lee, and K.J. Chang, Phys.Rev.Lett. **87**,096803(2001).
- [37] P. Havu, T. Torsti, M.J. Puska, and R.M. Nieminen, Phys.Rev.B **66**, 075401(2002).
- [38] B.H. Hong, S.C. Bae, C.-W. Lee, S. Jeong, and K.S. Kim, Science **294**, 348(2001).
- [39] V. Rodrigues, J. Bettini, A.R. Rocha, L.G.C. Rego, and D. Ugarte, Phys.Rev.B **65**,153402 (2002).
- [40] A. Sperl, J. Kröger, N. Néel, H. Jensen, R. Berndt, A. Franke, and E. Pehlke, Phys.Rev.B, **77**,085422(2008).
- [41] M. Springborg and P. Sarkar, Phys.Rev.B **68**, 045430(2003).

- [42] F.J. Ribeiro and M.L. Cohen, Phys.Rev.B **68**, 035423(2003).
- [43] H. Ohnishi, Y. Kondo, and K. Takayanagi, Nature **395**, 780(1998).
- [44] J. N. Crain and D. T. Pierce, Science **307**,5710(2005).
- [45] J. Yan, Z. Yuan, and S. W. Gao, Phys. Rev. Lett. **98**,216602(2007).
- [46] A. Delin and E. Tosatti, Phys.Rev.B **68**,144434(2003).
- [47] M. Wierzbowska, A. Delin, and E. Tosatti, Phys.Rev.B **72**,035439(2005).

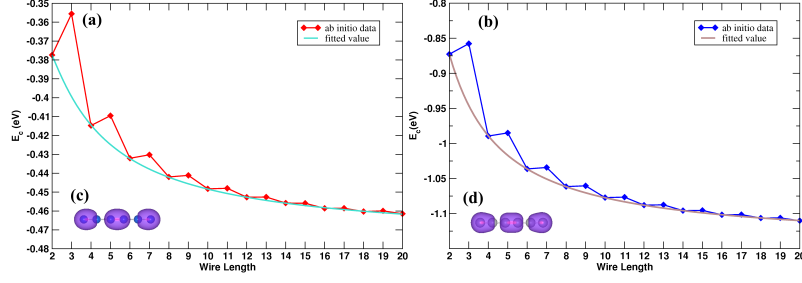


FIG. 1: (Color online) The cohesive energy E_c of (a) Na atom wires, and (b) Ag atom wires versus lengths. Fitting data are also shown in (a) and (b), respectively. HOWSs of (c) 6-atom Na wire and (d) 6-atom Ag wire are displayed, respectively.

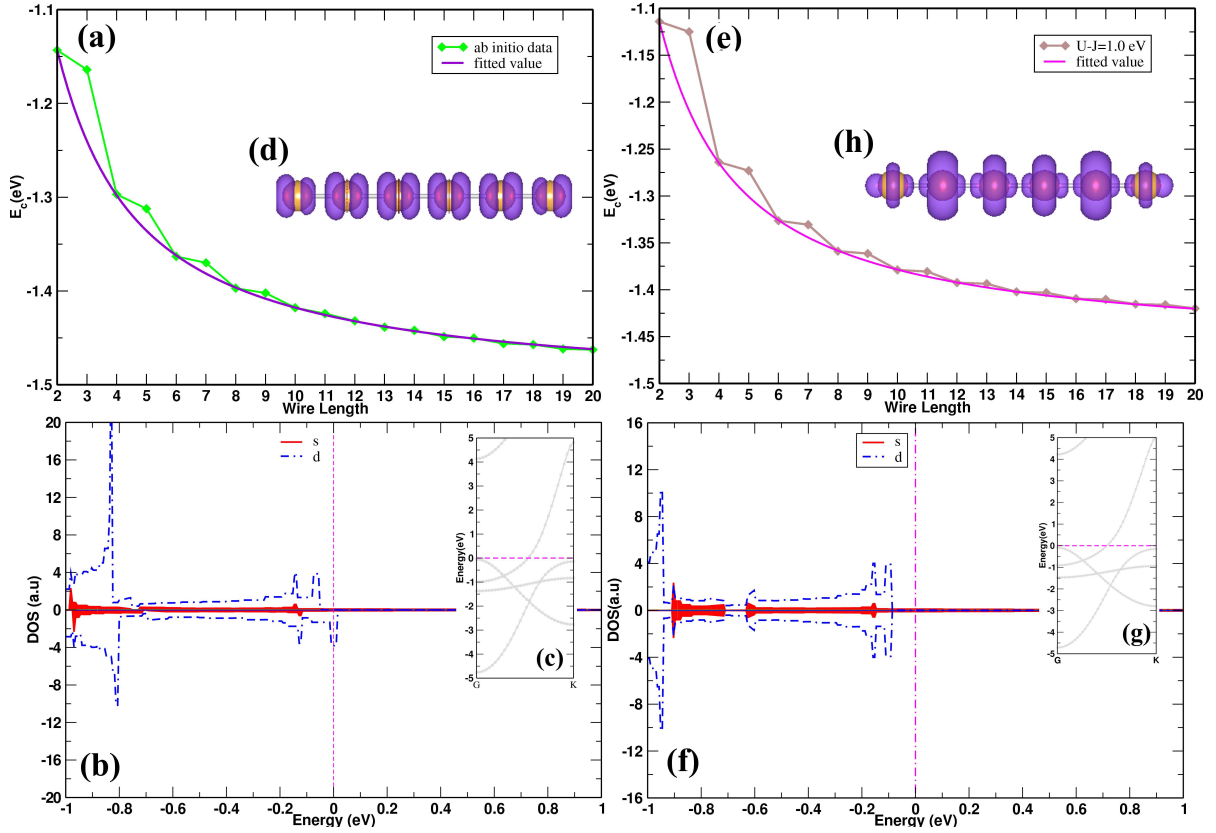


FIG. 2: (Color online) (a) The cohesive energy E_c of Au atom wires versus length, (b) and (c) are density of states(DOS) and bandstructure of the infinite Au wire, respectively. (e) The cohesive energy E_c of Au atom wires versus length by GGA+U calculations within $U_{eff} = U - J = 1.0$ eV, (f) and (g) are corresponding to DOS and bandstructure of the infinite Au wire. HOWS of 6-atom is then given in (h). In both cases, the Fermi level is the zero energy. Fitting data is also shown in (e).

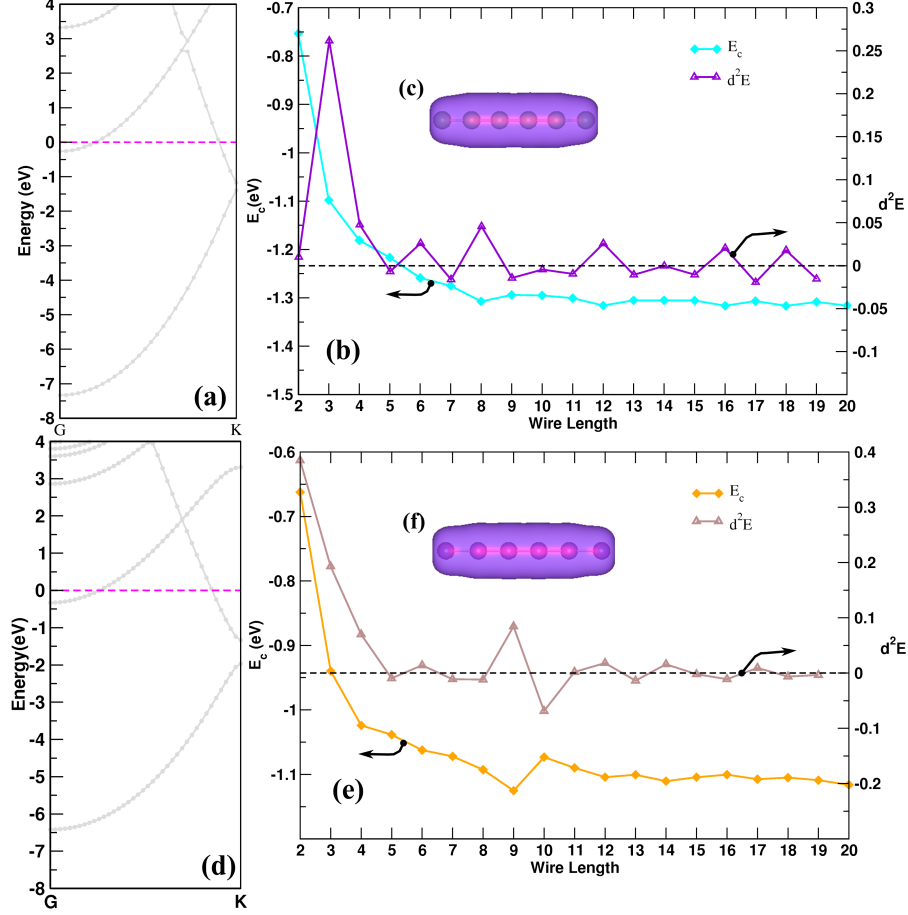


FIG. 3: (Color online) (a) and (d), bandstructures of the infinite Ga atom wire and In atom wire, respectively, and the Fermi level is set to the zero energy. (b) is the cohesive energy E_c of Ga atom wires versus length while (e) is that of In atom wires, and the second difference of E_c is presented together. HOWSs for 6-atom Ga wire and In wire are given in (e) and (f), respectively.

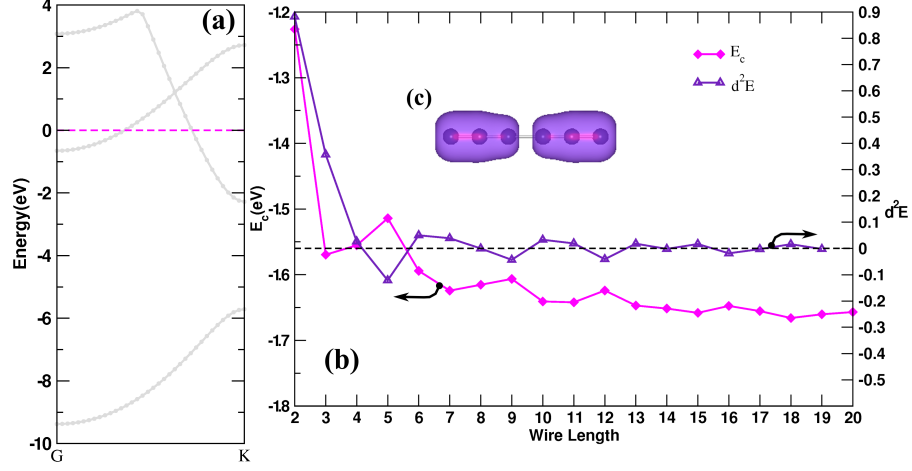


FIG. 4: (Color online) (a), the bandstructure of the infinite Pb wire, and the Fermi level is set to the zero energy; (b) The cohesive energy E_c of Pb atom wires versus lengths, together with the second difference of E_c , (c) is HOWS of 6-atom Pb wire.